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COBALT COLORS OTHER THAN BLUE

BY

R. T. STULL AND G. H. BALDWIN

INFLUENCES OF VARIABLE SILICA AND ALUMINA ON PORCELAIN GLAZES OF CONSTANT RO

BY

R. T. STULL

INVESTIGATIONS ON THE DIELECTRIC STRENGTH OF SOME PORCELAINS

BY

B. S. RADCLIFFE

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COBALT COLORS OTHER THAN BLUE.

By R. T. Stull and G. H. Baldwin, Ceramic Laboratories, University of Illinois.

INTRODUCTION.

The color imparted to a glass or glaze depends upon the kind of coloring oxide, the composition of the batch and the manner of heat treatment. It has been considered that cobalt is persistent in producing blue under all conditions. Since two or more distinct colors are obtainable from all other coloring oxides under different conditions, there seemed to be no logical reason why some color other than blue could not be obtained from cobalt oxide.

Since cobalt oxide has so persistently given blue colors under normal ceramic practice, it was evident that a departure in composition must be made from the ordinary commercial types of glazes if a color different from blue was to be developed from cobalt oxide.

A speculation as to the possible colors obtainable from cobalt oxide as the sole colorant is of interest. Cobalt salts in solution under certain conditions impart pink, while under other conditions the color imparted is blue. It, therefore, seemed possible to develop all the different shades from blue on one hand to pink or even light red on the other. The problem was to develop a type of glaze that would bring out the pink or red color if such were possible, and the key to the situation was found in blowpipe analysis. Magnesia and magnesium minerals containing cobalt, when powdered, moistened with a solution of cobalt nitrate and heated, give a pink color. Alumina and alumina minerals containing cobalt, when similarly treated, give blue.

This suggested a glaze high in magnesia and free from alumina. It was recognized that if such colors could be produced they would be of greatest value for low temperature work. Since a high content of magnesia imparts refractoriness to a glaze, it would be necessary to introduce a "softener" which would not influence the color toward the blue. Of the two "softeners," PbO and B_2O_3, tried in a preliminary test,[1] it was found that the former changed the magnesia-cobalt pink to blue, while the latter did not, hence B_2O_3 was selected as the "fluxing" or "softening" agent.

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[1] Vol. XII, Trans. A. C. S., pp. 707–708.

EXPERIMENTAL WORK.

First Group.—The first group of glazes was made in order to develop workable members over a range of temperatures. In this group the RO remained constant, the SiO_2 and B_2O_3 being variables. The limits covered were

$$\left.\begin{array}{l} 0.2\ Na_2O \\ 0.6\ MgO \\ 0.2\ CoO \end{array}\right\} 0 \text{ to } 1.0\ B_2O_3,\quad 1.0 \text{ to } 4.0\ SiO_2.$$

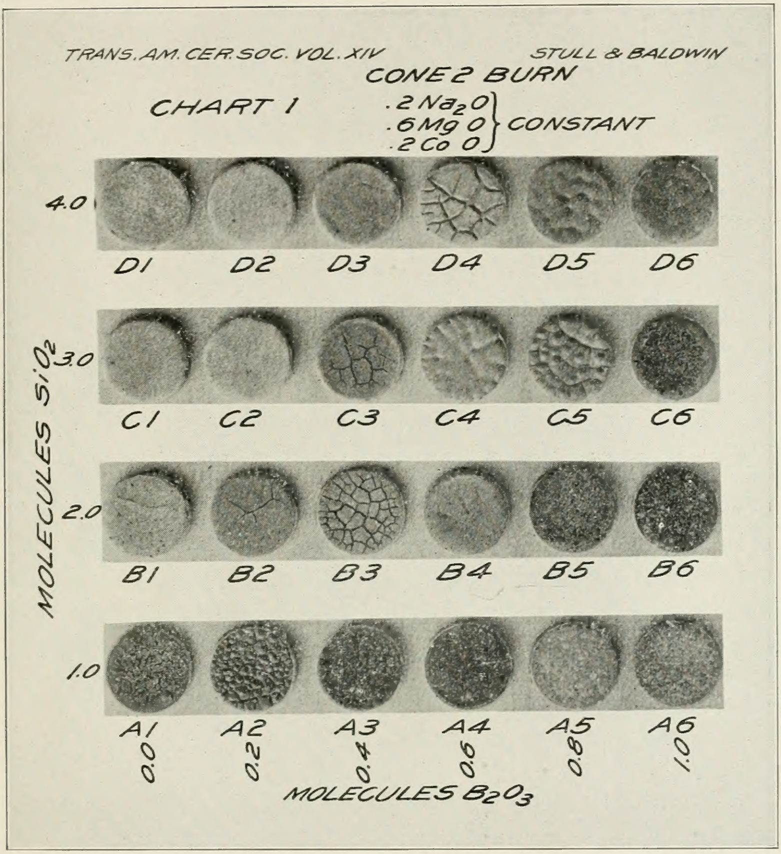
Twenty-four glazes were made in this group. The horizontal series are designated by letters and the vertical series by numbers (see charts). The formula and batch weights of the four corner glazes are:

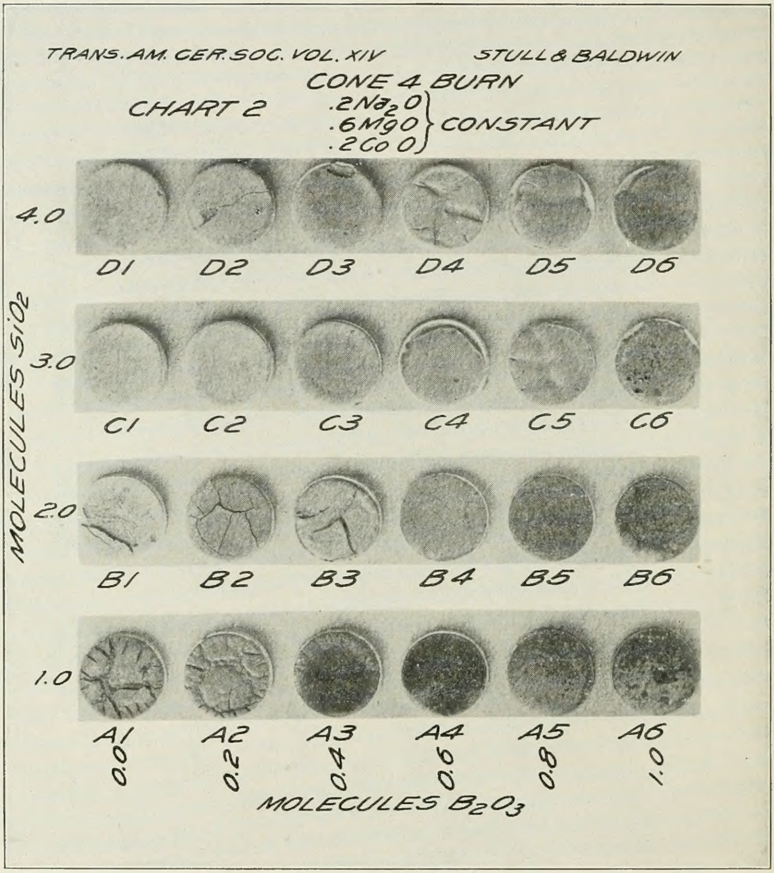
	Formulae					Batch weights				
	Na_2O	MgO	CoO	B_2O_3	SiO_2	Na_2CO_3	$MgCO_3$	Co_2O_3	$B_2O_3.3H_2O$	Flint
A-1	0.2	0.6	0.2	0	1.0	212	504	165	. .	600
A-6	0.2	0.6	0.2	1.0	1.0	212	504	165	1240	600
D-1	0.2	0.6	0.2	0	4.0	212	504	165	. .	2400
D-6	0.2	0.6	0.2	1.0	4.0	212	504	165	1240	2400

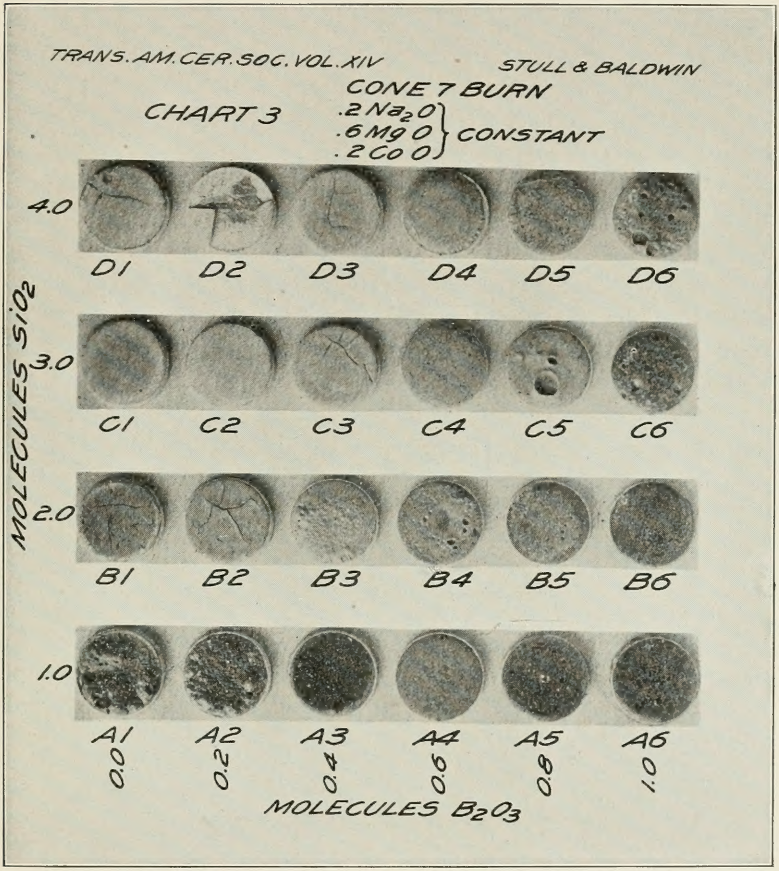
The four batches were weighed, ground dry for one hour, fritted and ground to pass 120 mesh. The different members in the group were made by blending the four extremes according to their combining weights.

Since the glazes settled rapidly and caked, it was found necessary to employ a "colloid" in order to induce flotation for application and adhesion on drying. Glucose, dextrine and glue were tested. The best results were obtained with 4–5 per cent. glue. Such large quantities of either glucose or dextrine were required in order to produce free flotation that the glazes cracked and curled up on drying. With glue, however, a high degree of flotation was obtained, and the glazes dried without cracking.

The glazes were applied in a thick coat on 2″ porcelain discs previously burned to cone 11. Three burns of this group were made, *viz.*, cones 2, 4 and 7 (Charts 1, 2 and 3). At cone 2


TRANS. AM. CER. SOC. VOL. XIV
STULL & BALDWIN
CONE 2 BURN
CHART 1
.2 Na_2O
.6 MgO
.2 CoO
CONSTANT
4.0
D1 D2 D3 D4 D5 D6
3.0
C1 C2 C3 C4 C5 C6
2.0
B1 B2 B3 B4 B5 B6
1.0
A1 A2 A3 A4 A5 A6
0.0 0.2 0.4 0.6 0.8 1.0
MOLECULES SiO_2
MOLECULES B_2O_3


TRANS. AM. CER. SOC. VOL. XIV
STULL & BALDWIN
CONE 4 BURN
CHART 2
.2 Na_2O
.6 MgO
.2 CoO
CONSTANT
4.0
3.0
2.0
1.0
MOLECULES SiO_2
D1 D2 D3 D4 D5 D6
C1 C2 C3 C4 C5 C6
B1 B2 B3 B4 B5 B6
A1 A2 A3 A4 A5 A6
0.0 0.2 0.4 0.6 0.8 1.0
MOLECULES B_2O_3


TRANS. AM. CER. SOC. VOL. XIV
STULL & BALDWIN
CHART 3
CONE 7 BURN
.2 Na₂O
.6 MgO
.2 CoO
CONSTANT
4.0
3.0
2.0
1.0
MOLECULES SiO₂
D1 D2 D3 D4 D5 D6
C1 C2 C3 C4 C5 C6
B1 B2 B3 B4 B5 B6
A1 A2 A3 A4 A5 A6
0.0 0.2 0.4 0.6 0.8 1.0
MOLECULES B₂O₃

(Chart 1) members C 6, B 5, B 6, A 5 and A 6 were well matured. A 4 and B 4 were well vitrified, presenting pleasing matte surfaces. Refractoriness increases on a line from A 6 to D 1. Member A 6 is a deep "red-violet" in color, showing more of the red than the blue. When we pass in any direction from A 6 upward or to the left, the red diminishes and the blue increases.

At cone 4 (Chart 2) the field of matured glazes has not materially broadened. A 4 and B 4 are still matte but their surfaces have changed from an "egg shell" texture to a promiscuously interlacing needle crystal, surface.

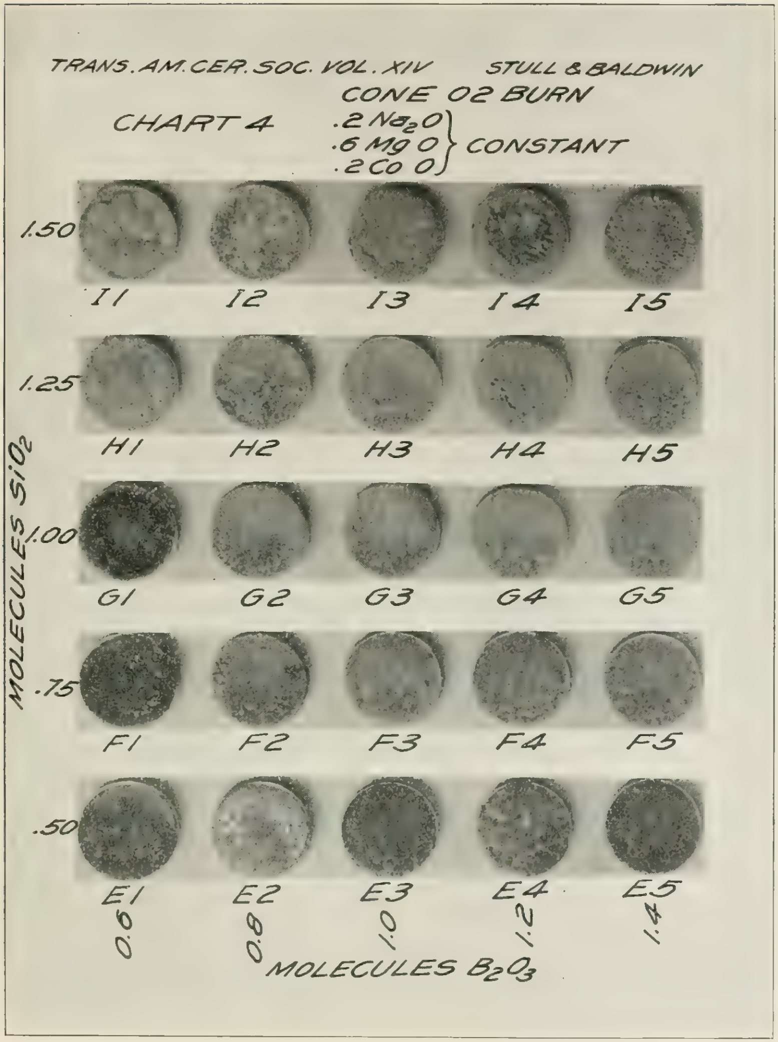
At cone 7 (Chart 3) the matured field has broadened only a little. A 5 and A 6 have reached a high state of fluidity, have flown down over the sides of the trials and are deep blue in color with a few spots of the red-violet here and there. These glazes show that they have attacked the body vigorously. In all three burns crystallization is quite prominent and brings out the red-violet color.

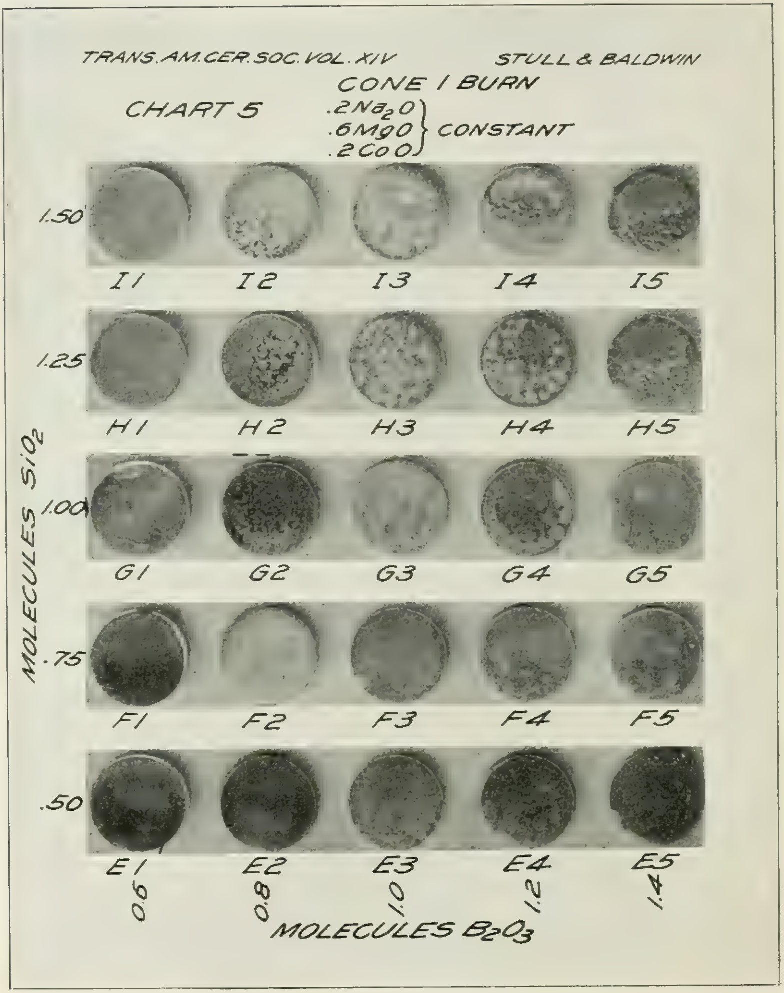
The results of this group indicate that a decrease in SiO_2 and an increase in B_2O_3 tends toward diminishing blue and increasing red, and that 2 molecules of SiO_2 as a maximum and 0.6 molecule of B_2O_3 as a minimum are the approximate limits in these directions for glazes that will mature well at or below cone 7.

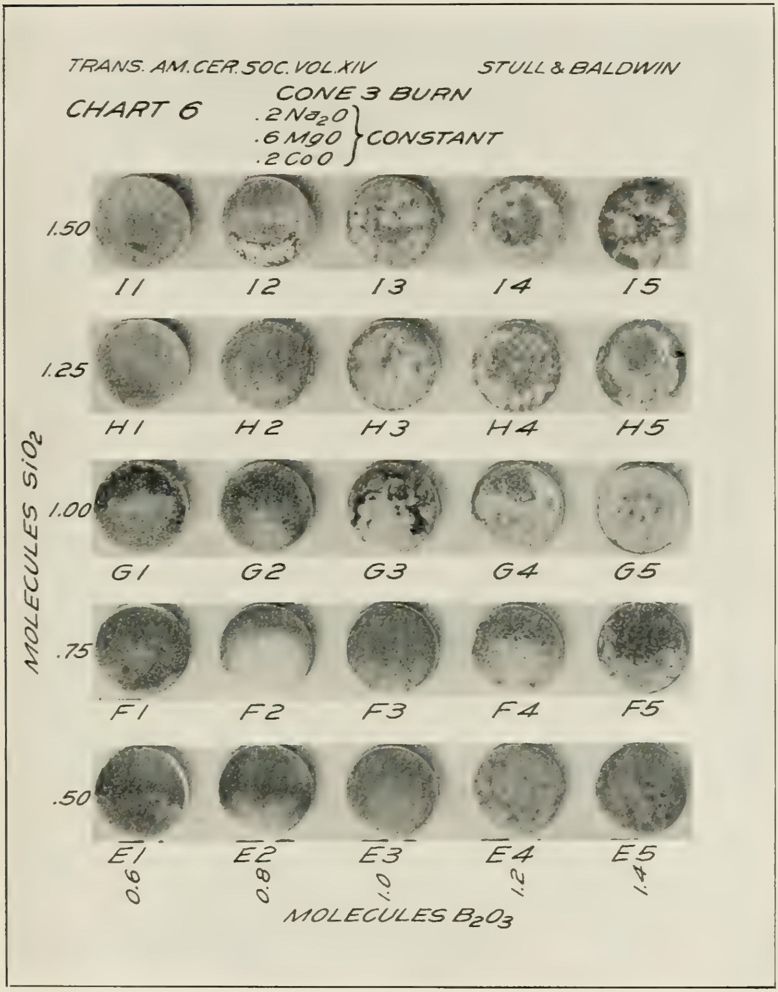
Second Group.—A second group was constructed with the idea of bringing out more of the red and less of the blue and to develop glazes maturing at lower temperatures. This group, in which the constant RO is the same as in the first group, covered the following limits:

$$\left.\begin{array}{l} 0.2\ Na_2O \\ 0.6\ MgO \\ 0.2\ CoO \end{array}\right\} 0.6 \text{ to } 1.4\ B_2O_3,\ 0.5 \text{ to } 1.5\ SiO_2$$

Twenty-five members were made, A 6 of the first group being stationed at the center and having the new nomenclature of G3. The members were blended from the four previously fritted extremes, the same as was done in the first group. The formulae and batch weights of the four extremes are:


TRANS. AM. CER. SOC. VOL. XIV
STULL & BALDWIN
CONE 02 BURN
CHART 4
.2 Na_2O
.6 MgO
.2 CoO
CONSTANT
1.50
I1
I2
I3
I4
I5
1.25
H1
H2
H3
H4
H5
1.00
G1
G2
G3
G4
G5
.75
F1
F2
F3
F4
F5
.50
E1
E2
E3
E4
E5
MOLECULES SiO_2
0.6
0.8
1.0
1.2
1.4
MOLECULES B_2O_3


TRANS. AM. CER. SOC. VOL. XIV
STULL & BALDWIN
CONE 1 BURN
CHART 5
.2 Na_2O
.6 MgO
.2 CoO
CONSTANT
1.50
I1 I2 I3 I4 I5
1.25
H1 H2 H3 H4 H5
1.00
G1 G2 G3 G4 G5
.75
F1 F2 F3 F4 F5
.50
E1 E2 E3 E4 E5
0.6 0.8 1.0 1.2 1.4
MOLECULES SiO_2
MOLECULES B_2O_3

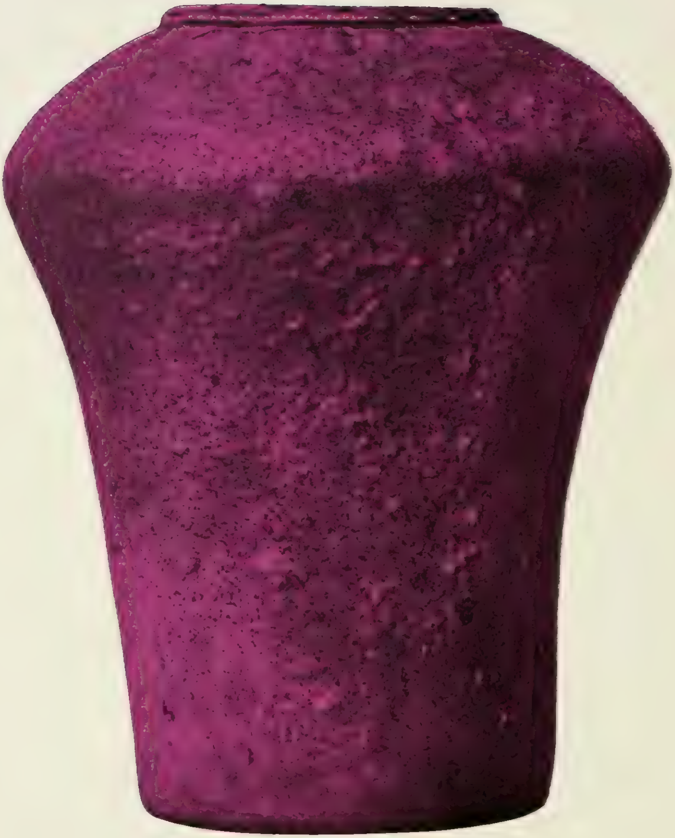

TRANS. AM. CER. SOC. VOL. XIV
STULL & BALDWIN
CHART 6
CONE 3 BURN
.2 Na_2O
.6 MgO
.2 CoO
CONSTANT
1.50
I1
I2
I3
I4
I5
1.25
H1
H2
H3
H4
H5
1.00
G1
G2
G3
G4
G5
.75
F1
F2
F3
F4
F5
.50
E1
E2
E3
E4
E5
0.6
0.8
1.0
1.2
1.4
MOLECULES SiO_2
MOLECULES B_2O_3

	Formulae					Batch weights				
	Na_2O	MgO	CoO	B_2O_3	SiO_2	Na_2CO_3	$MgCO_3$	CO_2O_3	$B_2O_3.3H_2O$	Flint
E–1	0.2	0.6	0.2	0.6	0.5	212	504	165	744	300
E–5	0.2	0.6	0.2	1.4	0.5	212	504	165	1860	300
I–1	0.2	0.6	0.2	0.6	1.5	212	504	165	744	900
I–5	0.2	0.6	0.2	1.4	1.5	212	504	165	1860	900

Three burns were made, *viz.*, cones 02, 1 and 3 (Charts 4, 5 and 6). The red-violet color was well developed in all cases except in vertical series 1, containing 0.6 B_2O_3, which remained persistently matte in all three burns. Crystalline patches appear in all pieces where well matured. The red-violet color is more prominent where crystallization has taken place. Decreasing SiO_2 and increasing B_2O_3 tends to throw the color toward the red and away from the blue the same as observed in the first group. Where the glazes are overfired, they have "run" considerably, attacked the body and give a clear blue. Occasionally a small group of red-violet crystals appear in a clear blue field.

Several of the glazes in this group were applied to porcelain bisque vases. In all cases where the glazes did not flow excessively or where crystallization appeared, the red-violet color was prominent. Where excessive flow took place the glaze remaining on the surface of the vase was a clear blue. In several cases where the glaze flowed down over fire clay "buttons" used as setters, the color of the glaze on these buttons was a dark green. The best glazes in the group are E 3, E 4, E 5, F 3, F 4, F 5, G 3, G 4 and G 5. Member F 4 appeared to be the best one in all three burns.

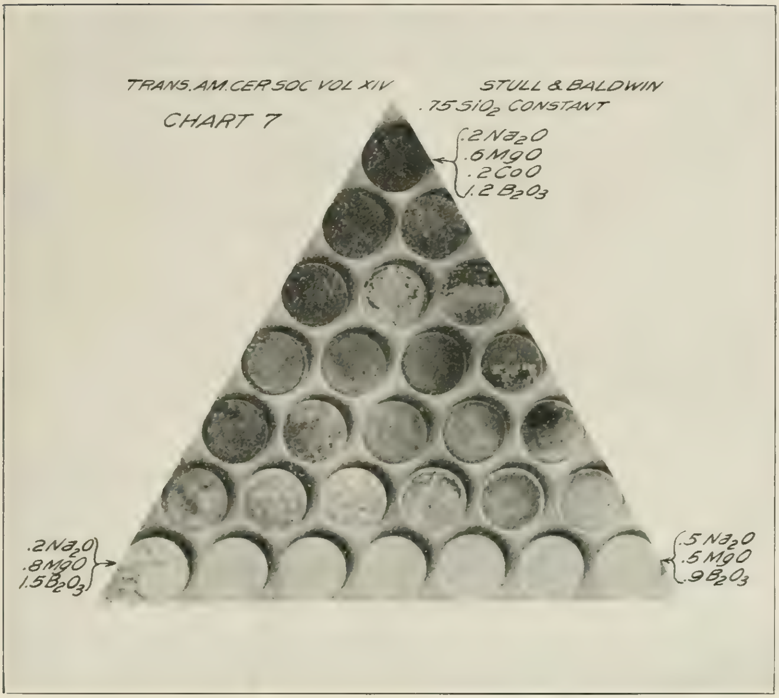
Third Group.—A third group was made in order to obtain lighter shades of the red-violet color. Since F 4 seemed to hold the color so persistently and showed a fair range of temperature, it was selected as the starting point. Lighter shades can be produced by blending F 4 with a similar glaze but containing no cobalt oxide. The first problem to solve was to produce such a glaze having the same heat range and fusibility as F 4. In order to save time it was decided to make a triaxial group (Chart



Purple Produced by Use of Cobalt

G-5 at cone 0 2

$$\left.\begin{array}{l}0.2\ Na_2O\\0.6\ Mg\ O\\0.2\ Co\ O\end{array}\right\}\ 1.4\ B_2O_3\quad 1\ Si\,O_2$$



7) by placing F 4 at the upper apex, and the two following colorless glazes at the lower corners:

$\left.\begin{matrix}0.2\ Na_2O\\ 0.8\ MgO\end{matrix}\right\}\ 1.5\ B_2O_3\ \ 0.75\ SiO_2 \qquad \left.\begin{matrix}0.5\ Na_2O\\ 0.5\ MgO\end{matrix}\right\}\ 0.9\ B_2O_3\ \ 0.75\ SiO_2$

The only constant member in the group is SiO_2 at 0.75 molecule.

The group was made by fritting the three extremes and blending as was done in the two preceding groups. Glazes were applied to porcelain discs and burned to cone 02.

Examination of the trials indicates that there is no difference in shade or intensity of color from a content of 0.1 CoO to 0.2 CoO. The glaze near the lower left corner is a dark lavender while the one near the lower right corner is clear blue. As the MgO and B_2O_3 decrease and Na_2O increases, the color tends toward blue. Wherever crystallization appears, the red-violet or a lighter shade tending toward lavender appears.

CONCLUSIONS.

The color violet is composed of equal intensities of red and blue. Most of the colors produced in the foregoing work lie between the violet and the red. A fusion of either soda or boric oxide and cobalt oxide gives blue. Cobalt silicate is blue. A mixture of magnesia and cobalt oxide heated to redness gives pink. The color darkens tending toward red as the temperature of calcination is increased; the color change, however, is not pronounced until very high temperatures are reached.

The red-violet, lavender or pink color is apparently due to some combination of magnesia with an oxide of cobalt. Decreasing MgO or increasing SiO_2 causes diminishing red and increasing blue. This would indicate that the silica has broken up the magnesia-cobalt combination, thus imparting the cobalt-silica blue.

Although a fusion of B_2O_3 and CoO gives blue, an increase in B_2O_3 in the foregoing glazes tends toward the red and away from the blue, indicating that the magnesia-cobalt red-violet color is not only stable in the presence of B_2O_3 but that the latter encourages the red by some action not definitely understood.

DISCUSSION.

Mr. Wilder: I would like to ask what would be the result of increasing the heat in the trials shown on the last diagram?

Mr. Stull: You would tend to get less of the red-violet or lavender and more of the blue. This is probably due to the fact that the glaze becomes very fluid as the temperature increases and attacks the body vigorously. The alumina taken up changes the color to blue. We intend to continue further and try what we call an insulating glaze, by biscuiting the porcelain at 05 to 02, then applying a glaze similar to the first one on the board, as, for example:

$$\left.\begin{matrix} x\mathrm{Na_2O} \\ y\mathrm{MgO} \end{matrix}\right\} z\mathrm{SiO_2}$$

In this glaze x, y and z must necessarily be determined experimentally in order to fit working conditions. After applying the insulating glaze to the soft biscuit, the body is to be vitrified at cone 11 or cone 12, then the colored glaze is to be applied and burned to maturity. In this way we hope to exclude alumina from the glaze.

Mr. Wilder: I would like to ask Professor Stull if he ever tried to make pigments by calcining the magnesia?

Mr. Stull: No, I have never done that.

Mr. Landrum: I made pigments by calcining iron oxide with magnesia; but I never decided whether there was a compound formed or not, nor whether there was a red-violet color from the magnesia and the ignition simply gave a more homogeneous pigment. I think there should be some trials made by igniting at a little higher temperature.

Mr. Stull: If the color so obtained were stable, it would work all right, but apparently these colors are very unstable during fusion in the presence of silica and alumina. It seems to me that it would be possible to make over-glaze colors along this line, if they are not fired too high and thus made too fluid. The white sample in the right-hand lower corner of the triaxial is very fusible and has attacked the body vigorously as it is pitted in places. Therefore, the over-glaze colors would have to be fired with caution, or so constituted as to possess a wide heat range.

Mr. Will: I make blue stains of various composition which in cone 8 and cone 10 fire turn out a pink-violet, a beautiful color, but the invariable experience has been that on being used as colors under a full glaze they turn to a deep blue. In other words, the red color is not stable except with a matte glaze. For instance, use same as a stain for a matte glaze, or a semimatte underfired, and you get a pink glaze. From this, purple glaze is often produced by overfiring, and on firing to a gloss the same piece will show a blue color.

Mr. Bruner: I would like to ask a question in regard to Chart 7. Professor Stull, do you wish to give us the impression that in the lower left-hand corner, the effect was due to low soda, high magnesia, high boric acid, and that if handled correctly, these glazes will give the pink color and on the other hand with low magnesia and low boric acid, the blue color comes out?

Mr. Stull: That is right.

Mr. Bruner: Are all those pieces exposed to just about the same heat or would you say their color was due to their position in the kiln? You do not mention anything about the fusibility and the possibility of the glazes being much more fused in one end of the kiln and the fact that when you have that condition it naturally leaves the color blue. On this piece (indicating number) you have a beautiful red-violet, as you call it, but inside it is blue. Even around the edges here you can see a little of the blue.

Mr. Stull: Underneath the red-violet glaze there is a thin film of blue next to the body, and where the glaze is thin the blue shows through. When crystallization takes place it brings out the red-violet color, and underfiring also brings out the characteristic red-violet color. On the inside of the piece, the thin glaze has attacked the body, thus giving the characteristic cobalt-alumina blue.

Mr. Will: I have applied one of these reddish blue colors to glazed Belleek ware and fired it again at glost kiln heat (cone 4–5) and there also one could not help noticing the phenomena of crystallization and the bringing out of red spots where underfired, while the balance of the piece showed a strong deep blue glaze with a high gloss.

Mr. Burt: I notice a number of these samples seem to show a distinct crystallization wherever the pink occurs, and I wondered whether Mr. Stull had examined it with that in mind. You get blue on the inside, but on the outer surface where you have sufficient surface glaze, you produce crystallization phenomena which develop this pink crystal. Is not the color something of a crystallization phenomenon?

Mr. Stull: It is true that the crystals do show the color, but the red-violet color is also developed in an underfired glaze and blue in an overfired glaze, or where the glaze is thin and has "fluxed into the body." On Chart 1, in the upper left-hand corner is the most refractory glaze in the group. It is as soft as chalk, yet it shows a light red-violet color. Alumina and cobalt together at a red heat will give a blue, while magnesia and cobalt will give pink. I do not know whether it is a chemical or a physical action that brings out the blue in one case and the pink in the other.

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INFLUENCES OF VARIABLE SILICA AND ALUMINA ON PORCELAIN GLAZES OF CONSTANT RO.

By R. T. Stull, Ceramic Laboratories, University of Illinois.

INTRODUCTION.

Porcelain glazes of the Seger cone formula type are the most inexpensive to produce synthetically, have a comparatively wide range of maturing temperature and give but few defects. These are offered as the principal reasons for the comparative meagerness of literature pertaining to investigations on glazes of this type.

Seger[1] gives the following as glaze formula commonly used for porcelain:

$$\mathrm{RO},\ (1 \text{ to } 1.25)\ \mathrm{Al_2O_3},\ (10 \text{ to } 12)\ \mathrm{SiO_2}$$

and for Seger porcelain[2]

$$\mathrm{RO},\ 0.5\ \mathrm{Al_2O_3},\ (4 \text{ to } 6)\ \mathrm{SiO_2}$$

Prof. Orton[3] gives the following limits for characteristic porcelain glazes:

$$\left.\begin{matrix} 0.1 \text{ to } 0.5\ \mathrm{K_2O} \\ 0.9 \text{ to } 0.5\ \mathrm{CaO} \end{matrix}\right\} 0.5 \text{ to } 1.25\ \mathrm{Al_2O_3},\ 4.0 \text{ to } 12.5\ \mathrm{SiO_2}$$

EXPERIMENTAL WORK.

In a study of porcelain glazes[4] of the cone formula type, two groups were made in order to illustrate the influences of variable silica and alumina. The first group covered the limits

$$\left.\begin{matrix} 0.3\ \mathrm{K_2O} \\ 0.7\ \mathrm{CaO} \end{matrix}\right\} 0.3 \text{ to } 1.0\ \mathrm{Al_2O_3} \left.\vphantom{\begin{matrix} 0 \\ 0 \end{matrix}}\right\} 1.8 \text{ to } 7.2\ \mathrm{SiO_2}$$

and comprised eight horizontal series, from A to H, containing eighty glazes in all.

The glazes in that portion of the field covered by the A to H series were made by blending the four extremes according to their combining weights. The formulae and batch weights of these extremes are:

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[1] Vol. II. Translations Seger, p. 705.

[2] Ibid., p. 706.

[3] Glaze lectures at Ohio State University, 1901–2.

[4] Work done by classes 1911 and 1912, University of Illinois.

Glaze	K_2O	CaO	Al_2O_3	SiO_2	Canadian feldspar	$CaCO_3$	Clay		$Al_2(OH)_6$	Ohio flint
							Eng. c.c. No. 7	Tenn. b.c. No. 7		
A–1	0.3	0.7	0.3	1.8	167.1	70.0	..	..	...	...
A–10	0.3	0.7	0.3	7.2	167.1	70.0	..	..	...	324.0
H–1	0.3	0.7	1.0	1.8	167.1	70.0	..	..	109.2	...
H–10	0.3	0.7	1.0	7.2	167.1	70.0	90.3	90.3	...	240.0

Glazes in the W to Z series were also made in the same manner with the exception that it was necessary to employ a frit in order to introduce the excess K_2O which could not be furnished by feldspar. The formulae and batch weights of the four extremes are:

	K_2O	CaO	Al_2O_3	SiO_2	Frit	Feldspar	$CaCO_3$	$Al_2(OH)_6$	Flint
W–02	0.3	0.7	0.25	0.6	85.6	...	50.0	23.4	...
W–6	0.3	0.7	0.25	4.8	21.4	125.3	65.0	...	198.0
Z–02	0.3	0.7	0.10	0.6	85.6	...	50.0	...	...
Z–3	0.3	0.7	0.10	3.0	85.6	...	50.0	...	144.0

Frit for the above:

$$\left.\begin{array}{l}0.6\ K_2O\\ 0.4\ CaO\end{array}\right\}0.2\ Al_2O_3\ 1.2\ SiO_2$$

Comb. wt. = 171.2

Feldspar = 111.4
K_2CO_3 = 55.2
$CaCO_3$ = 40.0

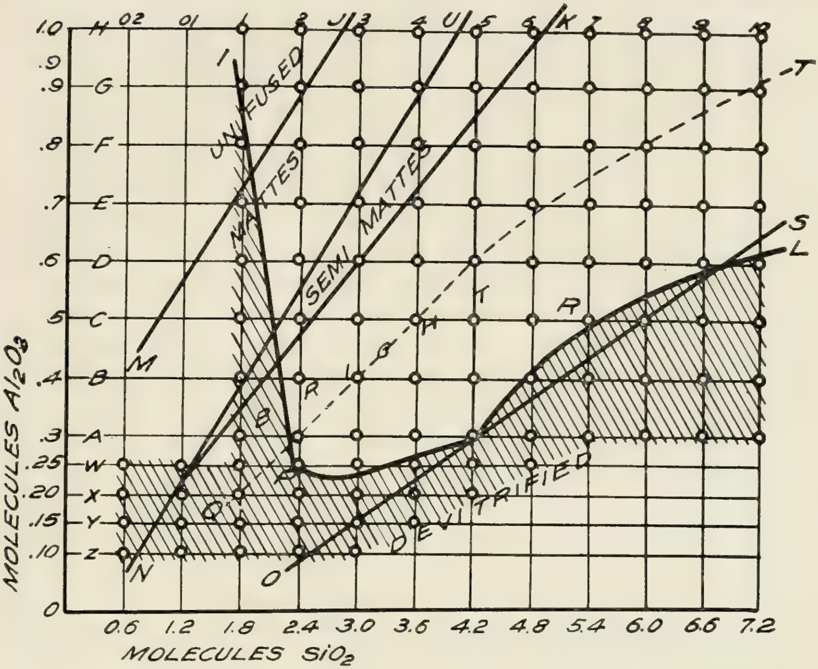
Crazing is comparatively rare in this type of porcelain glaze, due to the vitreous nature of the body and the similarity in composition of body and glaze. In order to intensify crazing and to locate that portion of the field in which it would be most likely to occur, the glazes were applied to porous, biscuit wall tile, which shrunk considerably but were still porous at the end of the burn.

The glazes were applied a little thicker than is customary in practice, and the trials set in tile saggers and burned to cone 11 in 36 hours. The results are shown graphically in Charts I and II.

DISCUSSION OF RESULTS.

On Chart 1, the molecular variations of silica are plotted along the abscissa and the molecular variations of alumina along the ordinate. The letters at the left denote the horizontal series and the numbers along the top the vertical series, so that each glaze is located by a letter and a number.

TRANS. AM. CER. SOC. VOL. XIV *CHART I* *STULL*



Since the RO for all glazes is constant, $\left\{\begin{matrix}0.3\ K_2O\\ 0.7\ CaO\end{matrix}\right\}$ the formula of any glaze can be read from the chart by referring to the ordinate for its alumina and to the abscissa for the silica. For example, the formula of E–5 is $\left\{\begin{matrix}0.3\ K_2O\\ 0.7\ CaO\end{matrix}\right\}$ 0.7 Al_2O_3 4.2 SiO_2. The alumina is constant in a horizontal series while the silica varies. In a vertical series the silica is constant and the alumina is the variable.

To the left of the line M J are the underfired mattes, and between M J and N U are the matured mattes. Between N U and N K are mattes showing a sheen or slight gloss and designated as semi-mattes. The bright glazes occur between N K and O S, and below O S the glazes are devitrified. The glazes are all crazes below the line I P R L and all sound above this line. The dotted line Q T passes through highest gloss of each series.

Beginning at the ordinate on Chart 1 and moving to the right parallel to the abscissa, it is observed that crazing and matte texture decrease with increase in silica, and that brilliancy increases up to the axis of highest gloss, Q T, beyond which brilliancy decreases, crazing increases and finally devitrification occurs.

Moving from the abscissa upward parallel to the ordinate, we see that increasing alumina has decreased crazing of glazes both high and low in silica, has decreased devitrification in high silica glazes, and increased matteness in low silica members.

A comparison of the influences of variable Al_2O_3 with those of variable B_2O_3 is of interest. It has been shown[5] that increasing B_2O_3 decreases devitrification and crazing in high silica glazes and increases crazing and decreases matte texture in low silica glazes. B_2O_3 and Al_2O_3 then function the same in high silica glazes but function oppositely in low silica glazes.

In Chart 2, the glazes are located by the molecular ratios of silica to alumina on the abscissa and by the total oxygen ratios on the ordinate. The molecular ratio of silica to alumina is independent of the total oxygen ratio, but the total oxygen ratio is partly dependent upon the silica-alumina ratio. Therefore, in plotting glaze groups similar to Chart 2, the evidence presented is influenced by one dependent and one independent variable. This must be borne in mind in drawing conclusions, otherwise they may be misleading.

The underfired mattes occur at 1, crazed mattes at 2, sound mattes at 3, semi-mattes at 4, crazed brights at 5, sound brights at 6, and glazes which are crazed and devitrified at 7. The line A B is the high gloss axis.

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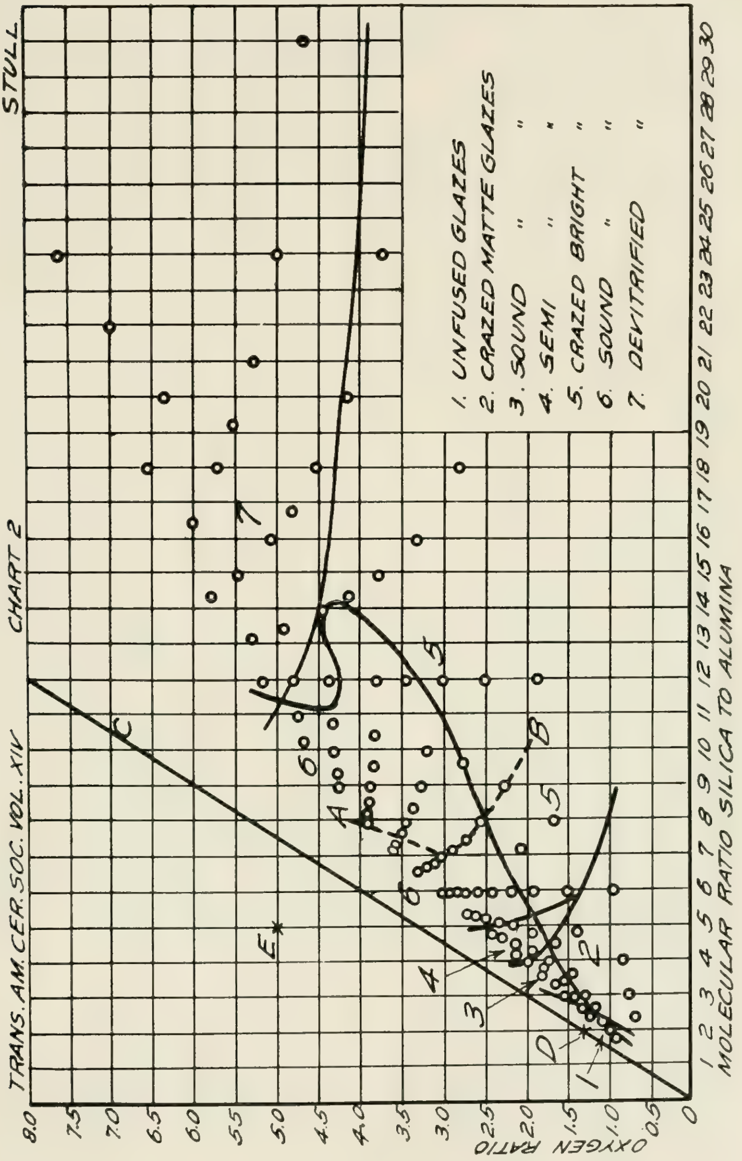
[5] "Opalescence and the Function of B_2O_3 in the Glaze," Trans. A. C. S., Vol. 12, pp. 119 to 137.


TRANS. AM. CER. SOC. VOL. XIV
CHART 2
STULL
1. UNFUSED GLAZES
2. CRAZED MATTE GLAZES
3. SOUND " "
4. SEMI " "
5. CRAZED BRIGHT "
6. SOUND " "
7. DEVITRIFIED "
A
B
C
D
E
1
2
3
4
5
6
7
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
OXYGEN RATIO
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30
MOLECULAR RATIO SILICA TO ALUMINA

The chart shows graphically that the matte glazes fall within narrow limits and that the bright glazes occur within wide limits. In the following table is given the ratio limits within which the different kinds occur:

	O. R.	$SiO_2 : Al_2O_3$
1. Underfired matte glazes (at cone 11)....	0.9–1.5	1.7– 2.7
2. Crazed matte glazes (at cone 11)........	0.6–1.6	2.4– 6.0
3. Sound glazes (at cone 11)..............	1.4–1.9	3.0– 4.0
4. Semi-matte glazes (at cone 11)..........	1.9–2.4	4.0– 5.0
5. Crazed bright glazes (at cone 11)........	1.4–4.4	6.0–24.0
6. Sound bright glazes (at cone 11)........	2.1–4.8	5.1–13.0
7. Crazed devitrified glazes (at cone 11)....	4.5–7.6	12.0–30.0

The trials show that the best bright glazes are found between oxygen ratios of 2.5 and 3.6 and silica-alumina ratios of 7 and 8.2. The best mattes occur between O. R.'s of 1.5 and 1.8 and silica-alumina ratios of 3.2 and 3.8. The high fire matte glazes given by Prof. Binns[6] fall within these limits.

As the alumina increases, the positions of the glazes approach the line passing through C to the origin O. This line represents a series of glazes having constant alumina, and variable silica. The general formula which satisfies any member in this series is RO ∞Al_2O_3, z SiO_2 in which z may vary from 0 to ∞. When z becomes infinitely large the formula may be reduced to the simple one of 1 Al_2O_3, y SiO_2. Dehydrated kaolinite, having a total oxygen ratio of $1.3^{1}/_{3}$ and a molecular ratio of 2, is located on the line O C at D.

The line O C is the dividing line between possible and impossible glazes. Take any point to the left of this line, as point E located by an oxygen ratio of 5 and a silica-alumina ratio of 5. From the general formula of the glaze 1 RO, x Al_2O_3, y SiO_2, the following equations are obtained:

$$\frac{2y}{1 + 3x} = 5 \qquad \frac{y}{x} = 5$$

in which $x = -1$ and $y = -5$. The formula then of a glaze to be located at E must be RO, -1 Al_2O_3, -5 SiO_2 which is impossible except mathematically. In the same manner, any other point to the left of O C may be shown to represent a glaze of the general formula 1 RO, x Al_2O_3, y SiO_2, in which x and y are negative.

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[6] Trans. A. C. S., Vol. VII, pp. 115–121.

As the dividing lines between the different glazes on Chart II approach the line O C, they curve upward, indicating that the higher the molecular content of alumina in the glaze the higher is the oxygen ratio for sound matte and bright glazes and that devitrification appears at a higher total oxygen ratio in high alumina glazes than it does in glazes lower in alumina.

The foregoing work seems to indicate that it is necessary to employ higher oxygen ratios for high alumina glazes (both bright and matte) than it is for low alumina glazes, and that the total oxygen ratio of 1 : 2 so often referred to as being best for bright glazes does not hold with, perhaps, the exception of low alumina glazes maturing at lower temperatures.

DISCUSSION WRITTEN AFTER READING THE ABOVE PAPER.

Mr. Staley: This paper is a fine example of careful and systematic work and of concise and graphic presentation of data. So well has the work been done that there is little room for discussion or comment.

From the standpoint of practical porcelain glazes, the first series, the A, B, C series, is of most interest. This may be divided into two groups of glazes: first, a group that can be made from the ordinary potter's materials, feldspar, whiting, clay and flint; and second, a group in which it is necessary to use $Al(OH)_3$, or its equivalent. The line dividing these two groups in Chart 1 runs in a straight course from the glaze with 0.3 Al_2O_3 and 1.8 SiO_2 to a point that would indicate a glaze with 1.0 Al_2O_3 and 3.2 SiO_2. It is plainly evident from the chart that the large majority of the glazes in the first group are good bright glazes at cone 11.

Inasmuch as Prof. Stull, for the sake of simplicity in blending, introduced considerable amounts of $Al(OH)_3$ into the high alumina glazes of the first group, we feel justified in predicting that if all the members of this group had been made from the materials ordinarily used by the potters. the boundaries of the matte and semi-matte areas would have been shifted somewhat toward the upper left-hand corner of the chart. We base this prediction on the well known fact that in high alumina glazes the introduction of a given amount of alumina as the free oxide, or its equivalent, has a more decided tendency to produce matteness than the introduction of an equal amount of alumina as clay.

Professor Stull has shown beautifully the facts that under certain conditions increase of alumina can stop crazing and increase of SiO_2 can cause crazing. Of course, both these statements are contrary to Seger.

The close relation between the boundary lines for crazing and devitrification in high silica glazes obviously suggests that the strains set up in the process of devitrification are responsible for the crazing. This is simply one more instance of crazing not caused by difference in coefficient of contraction

Inspection of the chart shows that a very simple rule can be devised for making a long series of good bright or matte porcelain glazes with this RO. Any raw glaze should have at least 0.05 equivalent of clay for mechanical reasons, so we will start with 0.35 Al_2O_3 and 2.40 SiO_2. Now by adding Al_2O_3 and SiO_2 to this glaze in the proportion of 0.10 equivalent of Al_2O_3 to 0.8 equivalent of SiO_2, we can make a long series of glazes lying close to the line of best bright glazes free from crazing. In terms of batch weights, this means that we can start with a glaze of the following batch: 33 feldspar, 14 whiting, $2^1/_2$ clay and 6 flint. To this batch we add clay and flint in the proportion of 1 part clay to 1.4 parts flint. To get the longest possible series of mattes, we simply drop out the flint from the above base glaze and make successive additions of clay. The members lowest in clay of this series would be liable to craze.

Mr. Stull: It seems to be a question as to whether all of the glaze ingredients go into solution or not. If complete solution takes place, the difference in texture of a glaze is not so marked whether the alumina has been added as $Al_2(OH)_6$ or introduced as clay. However, a high alumina content tends to increase viscosity which operates against diffusion and consequent homogeneity.

Although these matte glazes contain some alumina introduced as the hydroxide, the trials showed that the best mattes occurred between the O.R.'s of 1.5 and 1.8 as has been referred to. The high temperature matte glazes reported by Professor Binns in Volume VII fall within these limits. He reports his best matte as having an O. R. of 1.69. Although he used the regular potter's materials and fired at cones 8 and 9, it must be borne in mind that the replacement of clay by aluminum hydroxide and flint raises the maturing temperature Therefore, Prof. Staley is correct in his prediction, though it is probable that the lines would have been shifted only a short distance.

The fact that increase in alumina tends to overcome crazing was, to my knowledge, first brought out by Purdy and Fox in their work on "Fritted Glazes."

A study of results plotted graphically frequently reveals far more than mere description can do. In going back to the charts, a point is observed which might be of interest to the glass manufacturer. On Chart 2 it is observed that devitrification occurs at higher oxygen ratios as the alumina increases. Since sand is the cheapest material in the glass batch, there is an advantage in using all the sand that practice will permit for common window and bottle glasses.

Frequently the manufacturer of the common grades of glass is limited in the amount of sand he can use, owing to the liability of the glass to devitrify. If alumina can be introduced or its quantity increased in the glass, a larger per cent. of sand can be employed. Not only will the alumina tend to prevent devitrification, but will also tend to counteract increased viscosity due to increased silica. The fusion temperature then would be the principal limiting factor.

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INVESTIGATIONS ON THE DIELECTRIC STRENGTH OF SOME PORCELAINS.[1]

By B. S. Radcliffe, Van Asselt, Wash.

In the following work on porcelains, four problems were investigated for the purposes of determining:

1. The relation between dielectric strength and thickness.
2. The effect upon dielectric strength due to varied heat treatment during burning and cooling.
3. The value of fire clays as raw materials for high tension insulators.
4. Influence of lime on dielectric strength.

INFLUENCE OF THICKNESS.

The dielectric strengths of nearly all insulating materials (porcelain included) are considered proportional to the thickness. The strengths of varnished and impregnated paper insulators are exceptions. Since no experimental data was found pertaining to the relative dielectric strength to the thickness of porcelains, it was deemed advisable to make a few simple practical tests in order to determine this point for use in the work following. For this purpose, a body having the following composition, which vitrifies at cone 12, was made: Tenn. ball clay, No. 1, 15; No. Carolina kaolin, 20; Eng. china clay, 25; spar (Brandywine Summit), 20; flint (Ohio, 8 hr. grind), 20.

The body was prepared in the usual manner according to factory practice and the trials jiggered in the form of small crocks (Fig. 1) which could be nested closely so that all pieces would receive the same heat treatment.

The trials were made in different thicknesses, varying from 1.4 mm. to 7 mm., by adjusting the jigger tool. The trials were burned to cone $12^1/_2$ and punctured under transformer oil (Fig. 2), the voltage being increased gradually by a rheostat. As soon as the trial was punctured, the current was immediately broken.

The thickness at the point of puncture was measured by a micrometer. Five to ten trials made of the same thickness were punctured in each case. Whenever puncture took place

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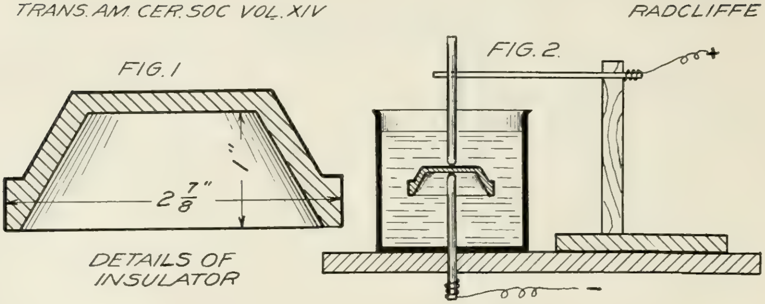
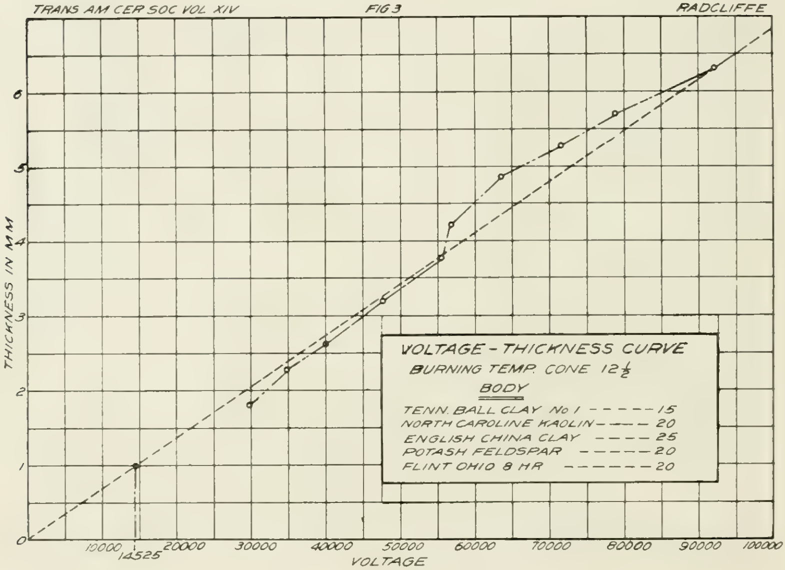
[1] An abstract of work done in 1909–10 in partial fulfilment of requirements for M. S. degree in Ceramics at the University of Illinois, under supervision of R. T. Stull.



through a flaw, the trial was rejected. The voltages required for puncturing sound trials of the same thickness were averaged, the thickness being plotted on the ordinate and voltage on the abscissa (Fig. 3).



Calculating the average puncture voltage per mm. thickness for all trials tested, assuming that the puncture voltage is directly proportional to the thickness, gives a voltage of 14,525. This point is plotted and the heavy dotted straight line passes from the origin through it. Owing to the fact that a voltage higher than 100,000 was not available, pieces over $6^{1}/_{2}$ mm. in thickness could not be tested. However, the limits covered exceeded the requirements in the future tests.

Some interesting results were obtained by puncturing the same test piece repeatedly in the same spot. One piece, 5.7 mm. in thickness required 83,800 volts, and was given a second test and punctured at 79,000 volts, a third test required 59,300, a fourth 51,200. When the trial was shifted to a new place, the voltage required to puncture it was 77,500. Other trials were treated in the same manner giving similar results. Repeated tests through the same line of puncture weakened the dielectric strength at that point, but not until several punctures did the porcelain become too weak to resist a fairly high voltage.

Apparently the current fuses the porcelain in passing. Upon breaking several pieces through the line of puncture a glassy appearance was always noticeable.

INFLUENCE OF VARIABLE HEAT TREATMENT.

There seems to be no data available pertaining to the effect of rate of burning and cooling upon the dielectric strength of porcelains. In order to throw some light upon this subject, four porcelain bodies were selected from the work of Bleininger and Stull on "The Vitrification Range and Dielectric Strength of Some Porcelains." These bodies are here designated by A, B, C and D. Besides these, E was made by blending the four.

Body	Georgia kaolin	Tenn. ball No. 1	N. Car kaolin	Eng. China clay No. 7	Potash feldspar	Ohio flint
A..........	50	..	..	..	40	10
B..........	..	55	..	..	15	30
C..........	..	..	55	..	25	20
D..........	..	..	..	60	20	20
E..........	5	9	27	18	23	18

Five more bodies were made similar to these except that soda feldspar replaced the potash feldspar by theoretical molecules. These bodies are designated as A1, B1, C1, D1, and E1.

Twenty trials were made from each of the ten bodies. These trials were divided into four sets, each set containing five trials made from each body. Each set was burned and cooled under different conditions. Set 1 was burned to cone 10 in six hours and cooled slowly in order to determine the effect of quick firing and slow cooling. Set 2 was burned to cone 13 in six hours after which air was passed through the kiln cooling the temperature down to cone 02 in one hour. The kiln was then allowed to cool slowly. Set 3 was burned to cone 10 in six hours then the temperature was gradually raised to cone 12 in an additional 14 hours, then carried rapidly to cone 17 and held for 2 hours. The kiln was then allowed to cool slowly. Set 4 was burned to cone 10 in 6 hours, gradually raised to cone 13 in an additional 18 hours and held for 20 hours. The kiln was then cooled down to cone 2 in five hours, then allowed to cool slowly.

C and C1 in the first burn showed 2 per cent. porosity but all the other bodies were well vitrified.

AVERAGE VOLTAGE PER MM. REQUIRED TO PUNCTURE TRIALS.

Body	Part 1, Cone 10	Part 2, Cone 13	Part 3, Cone 17	Part 4, Cone 13
A	13260	13120	12600	13070
A1	12840	13100	14300	13870
B	13400	13000	13500	13000
B1	14000	13640	13620	14160
C	10320	13960	12760	13180
C1	9180	13220	13820	13860
D	14510	13150	13680	14100
D$_1$	13400	13920	13100	13520
E	13550	13470	14660	12850
E1	13560	14820	14100	13860

The tests show that there is not a very wide difference in the dielectric strengths of the different bodies or in the manner of heat treatment. By taking the average puncture voltage per mm. for each different body for the four different burns (excluding C and C1 which were porous in the first burn), we have the following table which shows that the soda feldspar bodies have higher dielectric strengths than the corresponding potash feldspar bodies in all cases except in bodies D and D1 in which case D shows a higher dielectric strength than D1.

Potash spar bodies	Average voltage per mm.	Average voltage per mm.	Soda spar bodies
A	13012	13527	A–1
B	13225	13855	B–1
C	13300	13633	C–1
D	13867	13485	D–1
E	13632	14185	E–1

In order to get a comparison of the effects of variation in heat treatment, the average voltage per mm. is taken of the ten bodies for each of the four different burns. In averaging the first burn, bodies C and C1 are rejected on account of their porosities. The percentage variation between maximum and minimum puncutre voltages is less than 0.55 per cent. showing that the dielectric strength was substantially unaffected by the variations in burning and cooling from cone 10 to cone 17.

Burn	Cone	Average puncture voltage per mm.
Part I................	10	13569
Part II................	13	13540
Part III................	17	13614
Part IV................	13	13547

FIRE CLAYS AS RAW MATERIALS FOR HIGH TENSION INSULATORS.

The trade demands a white porcelain body for high tension insulators. Frequently a dark colored glaze (usually brown) is called for. If a colored body could be employed containing a high per cent. of fire clay, a cheaper body and a more uniform color of glaze would be the result. Insulators made from No. 2 fire clay or stoneware clay do not show a high dielectric strength. These clays vitrify at or near cone 8 while the white high tension porcelain insulators vitrify around cone 12.

In order to obtain bodies which would vitrify near cone 12, three fire clays were blended triaxially (Fig. 4). The three fire clays selected were: Olive Hill flint fire clay (calcined); Olive Hill No. 1 plastic fire clay; Bloomingdale[2] No. 2 plastic fire clay.

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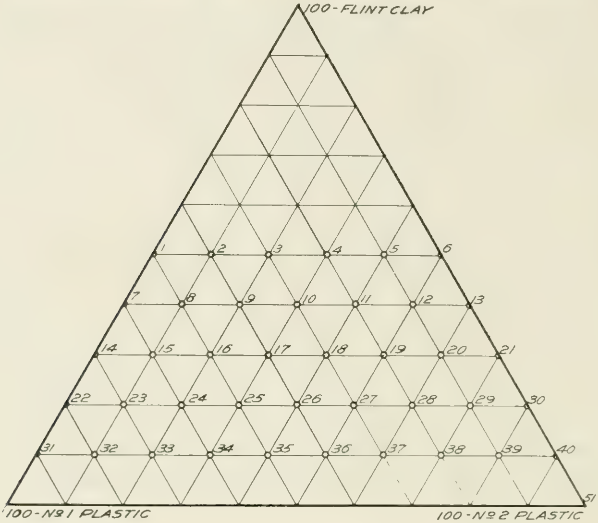
[2] An excellent stoneware clay, vitrifying at cone 8.

FIG 4

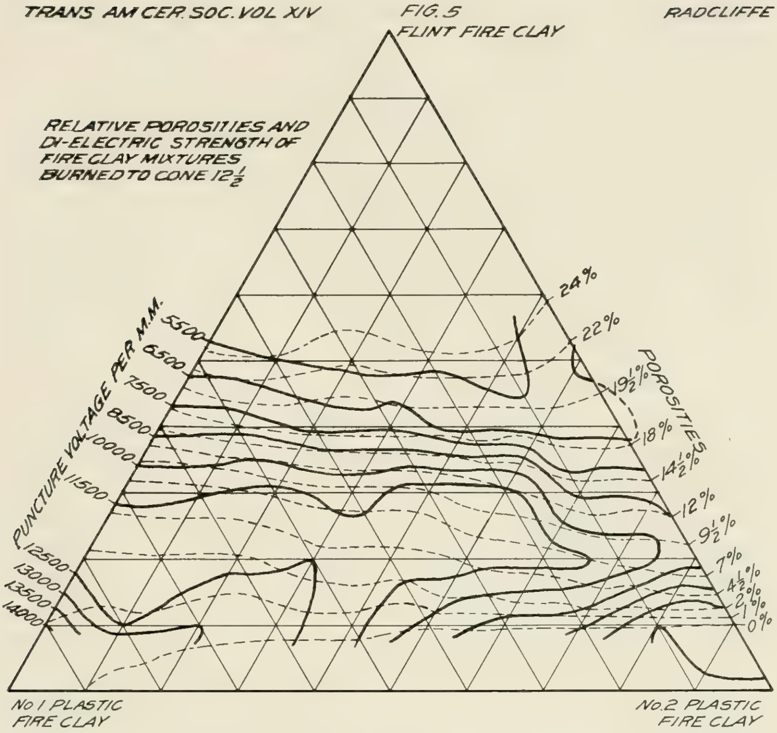


Five trials of each body were made and burned to cone $12^1/_2$. The porosities and puncture voltages were determined and averaged. These results are plotted on the triaxial diagram (Fig. 5), the dotted lines representing porosities and the heavy solid lines puncture voltages per millimeter thickness.

The results show that 90 parts No. 1 plastic fire clay and 10 parts calcined flint fire clay give a body of the highest dielectric strength at cone $12^1/_2$, and even though this body had 1 per cent. porosity, it compares very favorably with the best white porcelains in strength, 14,000 volts per mm. being required to puncture it.

When No. 2 fire clay or stoneware clay replaces the No. 1 plastic clay, the flint clay remaining constant, the dielectric strength is lowered even though the porosity is lowered at the same time.

Bodies containing 50 per cent. or more of No. 2 clay showed evidences of a "bleb" structure, which weakened them, causing them to puncture at a low voltage. The substitution of 10 per cent. No. 2 clay for No. 1 in body 31, which gives body No. 32,



did not materially lower the porosity, yet it lowered the puncture voltage from 14,000 to 12,500.

Trials which were subsequently made from bodies 14, 22 and 31 and burned to cone 14 gave a porosity for 14 of 1.34 and a puncture voltage of 13,600 per mm. The porosity of No. 22 was 0.08 and its puncture voltage 14,100 per mm. Porosity of No. 31 was zero and its puncture voltage 14,600, an increase in voltage of 600 for a decrease in porosity of 1 per cent. The white porcelain body of highest dielectric strength found in the foregoing work is the soda feldspar body E1, giving a puncture voltage of 14,820 per mm. in the part II burn. The potash feldspar body of highest dielectric strength is D, showing a puncture voltage of 14,660 in the part III burn.

In so far as dielectric strength is concerned, the foregoing evidence indicates that vitrified bodies made from refractory fire clays stand on an equal footing with white porcelains for high tension insulators.

Good colored high tension insulators can be made from a body composed of No. 1 plastic fire clay (part of which may be calcined) and a small amount of feldspar to assist vitrification. The use of flint fire clay in the body lowers the dielectric strength by increasing porosity through its refractoriness. The plasticity, working properties and shrinkage of a fire clay body can be controlled much better than white bodies and at the same time, it would be cheaper in composition.

INFLUENCE OF LIME ON DIELECTRIC STRENGTH.

In order to determine the effect of lime upon the dielectric strength of porcelain, the following bodies were made in which $CaCO_3$ was used to vitrify the bodies in place of feldspar. Part of the clay was calcined in order to control working properties. The trials were burned to cone 14 and porosities and puncture voltages determined. These results are given in the following table.

Body	Tenn. ball C. No. 1	N. Car. kaolin	Ohio flint	Calcined N. Car. kaolin	$CaCO_3$
F	10	45	22	23	0
F1	10	45	22	22	1
F2	10	45	22	21	2
F3	10	45	22	20	3
F4	10	45	22	19	4
F5	10	45	22	18	5
F6	10	45	22	17	6
F7	10	45	22	16	7
F8	10	45	22	15	8

The results show that 6 per cent. $CaCO_3$ has produced a non-porous body at this temperature which does not show a high dielectric strength, and that each increase in CaO has increased the dielectric strength. F5 containing 5 per cent. $CaCO_3$ has a porosity of 12.84 per cent. F6 shows that an increase of 1 per cent. of $CaCO_3$ has lowered the porosity to almost zero.

Body	Per cent. porosity	Average voltage per mm.	Body	Per cent. porosity	Average voltage per mm.
F	28.02	..	F4	12.65	..
F1	27.60	..	F5	12.84	5000
F2	20.52	..	F6	0.05	6000
F3	17.81	..	F7	0.03	6700
			F8	0.06	8000

When the puncture tests of F6, F7 and F8 are compared to those of feldspar porcelains of the same porosities and burned at the same temperature or even a little lower, it is observed that the dielectric strengths of the feldspar porcelains are from one and one-half to twice those of the lime porcelains.

CONCLUSIONS.

Conclusions which may be drawn from the foregoing work indicate that:

1. For all practical purposes, the dielectric strength is proportional to the thickness of the porcelain, which is in confirmation of that assumption.

2. Rapid burning or slow burning, rapid cooling or slow cooling do not materially affect the dielectric strength of high tension insulators so long as such treatment does not develop blebs, cracks or other flaws.

3. The average of all tests made in this work showed that the molecular substitution of soda feldspar for potash feldspar in a porcelain decidedly increased the dielectric strength.

4. High-grade fire clays are capable of making high tension insulators giving as high a dielectric strength as the average potash feldspar porcelain vitrifying at the same temperature.

5. The substitution of a stoneware clay for No. 1 plastic fire clay lowers both the maturing temperature and the dielectric strength.

6. A body made vitreous by the use of lime without feldspar gives a porcelain of low dielectric strength.

DISCUSSION.

Mr. Purdy: I note that he has a series in which calcium carbonate is varied against calcined clay. An explanation of the philosophy of a substitution of such unlike materials would be of interest.

I note also that he reports that a piece which has already been punctured will show a lower but relatively high strength when tested the second time at the same point and the same high strength when the same test piece is punctured at a new point. The only fact of value in these observations is the efficiency of oil as a non-conductor. When puncturing under oil the hole thus caused is filled with oil and not by glass as Mr. Radcliffe thinks. You can not re-test a punctured piece in the air as they did in the oil. In fact they could not have tested those shallow pieces in the air at all because of arcing around. Their data, therefore, on these two points is of value only for insulation under oil. Their conclusion should have been that their porcelain test pieces had but little, if any, better dielectric strength than did the oil they were using.

Prof. Stull: In order to satisfy Prof. Purdy's interest regarding the replacement of calcined clay by calcium carbonate, I will say that the calcined clay was employed merely for controlling the working properties and drying shrinkages of the bodies, as was mentioned when the paper was read. No attempt whatever was made to get a comparison of the bodies by variable lime-calcined clay. The object in view was merely to obtain vitreous bodies by using lime without resorting to additions of feldspar, and to compare the dielectric strengths of these lime bodies with those of feldspar bodies previously made.

There is no "hole" left after the porcelain has been punctured. Several of these crock shaped test pieces, after puncturing, were used as convenient receptacles for calcining small samples of kaolin at 1000° C. At this temperature the oil was completely burned off. Some of these trial pieces were broken through the line of puncture after they had served their purpose in calcining clay and these pieces showed plainly that the "hole" was filled with a glass.

Mr. Radcliffe shows that repeated puncturing through the same spot gradually weakens the dielectric strength. If puncturing leaves a hole and this hole is filled with oil, then why would not repeated puncturing after the first give the same voltage readings for puncturing the column of oil filling the hole?

The use of the oil bath is merely to prevent arcing. If the trial pieces had been made of suitable size and shape to prevent arcing when tested in air, there is no reason why they would not have shown the same dielectric strengths in air as they did in oil.

The results are comparative whether the porcelains are tested in air or in oil. Either set of conditions would show the porcelains of highest dielectric strength.

NOTES PREPARED AFTER READING THE PAPER.

Mr. Minneman: This paper by Mr. Radcliffe is a valuable addition to our ceramic literature, for the reason that so little experimental data is available along these lines.

I think, however, that certain of his conclusions are drawn too directly from his actual results, neglecting other conditions which are bound to enter in.

In regard to the dielectric strength of soda-feldspar *versus* potash feldspar, Mr. Radcliffe says: "The soda feldspar bodies have higher dielectric strengths than the corresponding potash feldspar bodies" and "The average of all tests made in this work showed that the molecular substitution of soda feldspar for potash feldspar in a porcelain decidedly increases the dielectric strength." However, upon looking over the individual test results, it is seen that in eleven cases the corresponding soda feldspar bodies show higher dielectric strength while in the remaining eight cases the corresponding potash feldspar bodies show the higher dielectric strength. Averaging the dielectric strengths of all the soda feldspar bodies and all the potash feldspar bodies, we find the soda feldspar bodies have only about 2.5 per cent. higher dielectric strength than the corresponding potash feldspar bodies. This appears to be a decided increase in the dielectric strength, but when it is remembered that, in the method used in testing, voltage readings accurate to several per cent. are almost impossible, and variations up to 10 per cent. are quite possible, this difference of 2.5 per cent. seems almost negligible.

The voltage readings in these tests were taken, I understand, from a voltmeter placed across the low tension side of the transformer, getting a calibration curve between the volts primary and volts secondary by means of a needle gap in the high tension side. The readings could, therefore, not be more accurate than readings from the needle gap which would be from one to four per cent., depending upon the experience of the observer. Add to this numerous uncontrollable variables, such as varying weather conditions, growth of charge in the circuit, variation in wave form and the time element in testing and it is evident that a wide divergence is quite possible.

That such a variation occurs, may be seen from the results obtained by Messrs. Bleininger and Stull, Vol. XII, Trans. A. C. S., p. 638, who made tests on the same porcelains fired at approximately the same heat treatment and tested with the same, or a very similar, apparatus. Comparing their results on the same trials and with Radcliffe's results we find variations up to 25 per cent.

Considering these points, I should say that Mr. Radcliffe's results tend to show that the dielectric strength of a porcelain is the same whether made from soda feldspar or potash feldspar so long as the porcelain is well vitrified and dense.

In regard to the use of lime, Mr. Radcliffe concludes that "a porcelain made vitreous by the use of lime without feldspar gives a porcelain of low dielectric strength."

It must be remembered that Mr. Radcliffe replaced his feldspar with lime and calcined china clay, thereby making a body of an entirely different structure. It is evident that a body made up with calcined clay and lime in place of feldspar would behave quite differently, due to the lesser distribution of the lime particles and the resulting differences in fusion, just as a body made up with equivalent amounts of sodium carbonate and calcined clay would differ from a body made up with soda feldspar. Had the clay and lime been fritted and ground until a homogeneous mixture was reached before being used in the porcelain, I think that entirely different results might have been obtained. I agree with Bleininger and Stull that dielectric strength "depends more upon sound vitrification and good mechanical structure than upon chemical composition."

Mr. Radcliffe's results do, however, show that lime used in porcelain in this way materially shortens the firing range.

The great volume of high voltage porcelain is not used under oil but in air and tests under oil often give entirely different results than do air tests. It is particularly noticeable that a porcelain not completely vitrified and having considerable absorption shows up very well when tested under oil, but breaks down much earlier when tested in air with the bottom of the test piece placed in water as is done in commercial tests.

Mr. Radcliffe mentions the puncturing of a piece under oil repeatedly in the same spot. When testing porcelain in air, after puncture once takes place there is a continuous flow of the current, and the piece ceases to act as an insulator. When testing under oil, however, this repeated puncture at a lower voltage often takes place, which leads me to believe that the oil protects the punctured spot sufficiently to give considerable insulation after the first puncture.

Consequently I should say that tests made in air, more nearly approximating conditions under which high voltage porcelain is used commercially, would be of much more practical value.

Prof. Stull: The question of experimental errors enters into all research work of this character. In theory, however, there is such a thing as absolute accuracy. The value of research work depends largely upon the accuracy in executing the work and the extent to which experimental errors are avoided or eliminated.

One of the greatest sources of error which Mr. Minneman failed to mention is due to variations in structure of different pieces made from the same body. It is impossible to eliminate minute air bubbles and to mould two pieces of porcelain so that they will have identically the same structure.

Where it is impossible to eliminate experimental errors or to deduct such errors by calculations from known data, it is customary to make several tests and to consider the mean average as a means of reducing such errors to a minimum.

As has been mentioned, Mr. Radcliffe made from five to ten different puncture tests for each different body under each different set of conditions, excluding all trials in which flaws due to moulding were apparent and taking the mean average of apparently sound pieces.

Mr. Minneman states that "it is seen that in eleven cases the corresponding soda feldspar bodies show higher dielectric strength while in the remaining eight cases the corresponding potash feldspar bodies show higher dielectric strength."

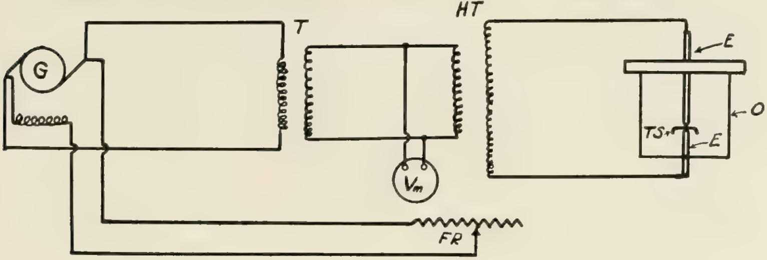
It was stated in Mr. Radcliffe's paper when read that "bodies C and C1 are rejected on account of their porosities" (in the first burn). Since these two bodies are porous they are not at all comparable with the others which were well vitrified, hence, it is legitimate and proper to exclude them from the calculations. Excluding C and C1 in the first burn, it is observed that the comparison is as twelve to seven, as Mr. Minneman has evidently made an error in count.

Since five trials of each porcelain for each of the four burns were tested, the average puncture voltage per mm. (excluding C and C1 in the first burn) is calculated on ninety-five trials punctured for each type of porcelain. Taking the average of such a large number of tests tends to give an accurate comparison.

The physical properties of ceramic mixtures depend upon composition and method of treatment. The treatment of the potash feldspar porcelains and the corresponding soda feldspar ones were carried out as nearly alike as possible. Since the two different kinds of feldspars are bound to exert some differences upon the physical properties, and one of these physical properties is "dielectric strength," it is more logical to conclude that the substitution of soda feldspar for potash feldspar has increased the dielectric strength since this conclusion is backed by the average results of ninety-five puncture tests of each of the two types of porcelain.

Mr. T. H. Armine: The puncture tests made upon the porcelains referred to in Mr. Radcliffe's paper were made under my supervision in the Engineering Experiment Station at the University of Illinois.

The accompanying sketch shows the connections used in



TRANS. AM. CER. SOC. VOL. XIV FIG. 6. RADCLIFFE

the test: G is a generator of 60 kilowatts capacity which produces practically a sine wave of electromotive force. T is a transformer stepping the voltage of the generator up by a four to one ratio. HT is a transformer of 10 kilowatts capacity which is designed to step from 440 up to 100,000 volts. FR is the field rheostat of the generator by means of which the high tension voltage was varied. O is a stoneware jar having a brass electrode, E, inserted through a hole in its bottom. A similar electrode, E^1, was arranged in such a manner that it was brought in the same straight line as E and so that it could be pulled up away from E to permit of putting the porcelain sample TS between the electrodes.

The first procedure was to obtain a calibration curve of the apparatus. The connection was removed from the electrode E and E^1 and a needle gap was placed across the high tension side of the transformer. With various settings of the needle gap the voltage was gradually brought up by varying FR until the discharge took place across the gap, at which time the voltage on the low tension side of the transformer was read by means of the voltmeter Vm. In this way the relation between "volts primary" and "length of the needle gap" was obtained. Then by means of the well known A. I. E. E. curve between "distance between needle points in air" and "volts," the "centimeters width of needle gap" were translated into "volts secondary." This calibration was repeated several times and good checks were obtained so the average curve between "volts primary" and "volts secondary" was adopted as the calibration curve.

In making the puncture tests the connection was made as shown in the diagram, a porcelain test piece, TS, was placed between the electrodes and the stoneware jar O filled with transformer oil. The voltage was gradually brought up by varying FR until puncture took place, at which time the "volts primary" were read by means of the voltmeter Vm. By means of the calibration the curve "volt secondary," that is, the volts to produce rupture, could be obtained. In all the tests care was taken that the rate of increase in voltage was uniform for all samples.

In Mr. Minneman's discussion of this paper the question of accuracy of the results obtained is brought up. Since the calibration curve was obtained by reference to a needle gap it may be in error by as much as 4 per cent. Since it was made all in one day under as constant conditions of weather, etc., as possible and since several checks were made it is probable that the error in calibration is less than this. However great the error in the calibration curve is, it is a constant error and affects the reading only when considered as absolute values of voltage and does not affect the relative values obtained for the various samples. For instance, the tests upon soda feldspar *vs.* potash feldspar involve none of "the uncontrollable variables such as varying weather conditions, growth of charge, variation of wave form and time element," mentioned by Mr. Minneman. The values obtained for these two porcelains should be closely comparable even if the absolute values of voltage were seriously in error since the errors should be the same for both sets of tests.

Mr. Minneman also mentions that "when testing a porcelain in air, after puncture takes place there is a continuous flow of current and the piece ceases to act as an insulator." This same action takes place with tests under oil. At the instant of rupture the current follows the arc and continues to follow it as long as the voltage is on in the same way as it does with a test in air. A second application of voltage in the same spot does show that there is still considerable dielectric strength after the first puncture. This dielectric strength is not, however, due to the protective effect of the oil. The current which follows the arc fuses the porcelain and when the circuit is broken the fused porcelain solidifies in place, forming a glassy spot. Due, perhaps, to flaws and to the presence of foreign material such as carbonized oil, which probably prevents the formation of a homogeneous structure, the strength on second puncture is less than on the first. The voltage at which a sample will puncture the second time has, I believe, no relation to the real dielectric strength, *i. e.*, on first puncture, of the porcelain sample. I believe that the only serious effect of testing under oil would be with very poorly vitrified porcelains such as are obviously not fit for high tension insulators. In testing these porous porcelains comparable results possibly would not be obtained under oil.